

ISTC Project No. #1571P

**Synthesis of New Organic Semiconducting Polymer Materials
Having High Radiowave Absorption Rate**

**Final Project Technical Report
on the work performed from 12.01.2007 to 11.30.2008**

Life Sciences International Postgraduate Educational Center

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14. ABSTRACT: In the present project for the first time the polyaniline, polydifenilamine, polycarbazole of the set structure (including functional groups) and morphology of nano-sized particles with the optimal radiowaves absorption rate was elaborated. From the obtained semiconducting polymers, elastic and flexible composite materials including nano-composites were developed. We find out that the silicon compositions and nano-sized compositions have the highest adsorption properties. We suggest that the development of these nano- sized compositions and their derivatives is very promising from the point of obtaining new coating materials, having higher adsorption properties. However, in the framework of present project, our technical possibility did not allow us to study their adsorption properties at different frequency of modulated and non-modulated MW, as well as their multisided physicochemical and structural characteristics. For the study of MW adsorption properties of synthesised polymers film a new microcalorimetric and radiometric methods were elaborated. However, for obtaining more precise data on specific adsorption rate of MW at different frequency for different materials these new methods need the future modification. For estimation of the protective (shielding) properties of organisms from non-thermal biological effect of MW, two extrasensitive methods were used: a) luminicent method measuring the hydrogen peroxide (H ₂ O ₂) formation in shielded and non-shielded water samples and b) isolated snail heart muscle contractility. Thus, by performing the present project it was established the necessary theoretical chemo-technical basis for synthesis of aromatic polymers and for studying their MW adsorption properties from the point of public health. Further development of this project could allow to create and improve the technology of synthesis and properties of synthesised polymers that could be applicable for protection of electronic communications from unauthorized invasions, for companies producing mobile phones and, generally, radio electric equipment. Thin-film compositions could be used for camouflage of land, marine and air objects.					
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1. Brief description of the work plan: objective, expected results, technical approach

Objective

In this project, it is proposed to form the polymer films by using the synthesized near defectless polymers by vacuum evaporation, sedimentation from a solution and by electrochemical methods. Such films will be characterized in depth for structure, electrical conductivity and isolating properties by means of methods of structure analysis: NMR, IR, XPS, UV and visible spectroscopy, VEGA-1S microscope, kinetic, potentiometric, thermochemical and other methods.

Expected results

The new polymers - polyaniline, polyacetylene and polycarbazole of the set structure (including functional groups) and morphology of nanosized particles with the optimal radiowave absorption rate were developed.

For the first time it was shown the correlation between polymer structure and its ability for radiowave absorption, as well as was suggested a new method of synthesis of polymers with the optimal properties.

The obtaining nanosize composites absorbed the high frequency radiowaves of 8,2 and 260 GHz with the absorption rate up to 30 Db at the thickness of the films of 0,2-2 mm.

It is expected that the wide adaptation of these polymers for protection of the cells (living organisms) would enable their application for technological purposes and also for personal protection from MW radiation (including the mobile phone radiation).

The synthesis of new materials with the set properties has a number of peculiarities (conditions of synthesis, temperature, concentration of reagents, technical registration of the process), which wouldn't cause an unapproved synthesis of the production. The methods of materials synthesis with the set properties and estimation of structural peculiarities and defects would be protected by appropriate patents.

These investigations allowed the creation of improved materials for application in technique for protection of electronic communications from unauthorized invasions. The obtained nano-size composites absorbed in high frequency waves, at frequency of 8.2 and 260 GHz. The effective way of income receipt is the creation of our own manufacture, however the sale of licenses could also be considered. The preparation of patent application in collaboration with our partners is planned.

The results of the project would be of interest for companies producing mobile phones and, generally, radio electric equipment for increasing the safety of their production from the point of public health.

Technical Approach

The synthesis of polymers was carried out by oxidative polycondensation of corresponding amines, the process controlled by kinetic and potentiometric methods. The preparation of polymer films and plates was conducted by means of dispersion or vacuum sputtering.

The microcalorimetric and radiometric methods were used for determination of the absorption rate of MW radiation. The measurements was conducted by a device elaborated in the UNESCO Chair-LSIPEC

2. Method, Experiments, Theory etc.

The oxidation of the aniline and its derivatives is the key stage for the synthesis of the conjugated aromatic polyamines with semi conducting properties. However, very often due to the composite characteristic of the primary products of the tests, it is impossible to detect the structure of more composite products for the further condensation without knowing the content of the latter. From the chemical point of view it can be realized if we take into consideration the fact that even in the best conditions for the synthesis of aniline and other aromatic amines, more than ten reactions occur. Thus, the by-products which are the result of the above mentioned reactions are very active in the processes of the further polycondensation and, as a rule, integrate in the polymeric chain, creating a lot of structural heterogeneities, which are very difficult to estimate and have a strong effect on the properties of the final polymer [3-5a].

In the present work we studied the regularity and the mechanism of the synthesis of the aniline by persulphate ammonium in acid and tried to summarize the huge experimental material obtained in this field.

In previous works it was shown that during the chemical as well as electrochemical synthesis of the aniline it is formatted kation radical of aniline in water, which irreversibly dimerizes basically in N-phenyl 1,4 phenylenediamine (D) [3-5*]. The condensation of kation-radical is complicated by the possibility of the combination of head to head or end to end by the formation of benzidine and diphenylhydrazine. The latter is isomerized into benzidine in the acid medium and into azobenzene in the abundance of oxidizer [3]. Depending on the conditions of the synthesis the ratio of these products is changing within considerable limits. In moderate acid medium (pH – 1-3) it is mainly formulated dimer (D), in strong acid medium is formulated up to 25% benzidine, while in neutral and basic medium due to the high speed of deprotonation of the kation-radical the quantity of the azobenzene increases up to 10%.

Probably at the initial stage the formulated kation-radical stabilizes as a result of the formation of the complex with an abundance of aniline, thus the formation of the above mentioned by-products is regulated by the stability of the complex. The stability of the kation-radical complex with the aniline increases so much in the formic acid that at the initial stage of the synthesis of the aniline it is possible to record the signal electron paramagnetic resonance (EPR) [6].

We observed the increase of the concentration of kation-radical at the initial stage of the synthesis of the aniline till the formation of polymer. It can be observed when kation-radical is stabilized and probably dimer is obtained by the synthesis of the kation-radical complex with the monomer due to the chain mechanism. The formation of the charge transfer complex (CTC) between kation-radical and aniline is approved also by the appearance of peak at range of 420nm in UV specters of reactive medium at the initial stage of the synthesis of the aniline.

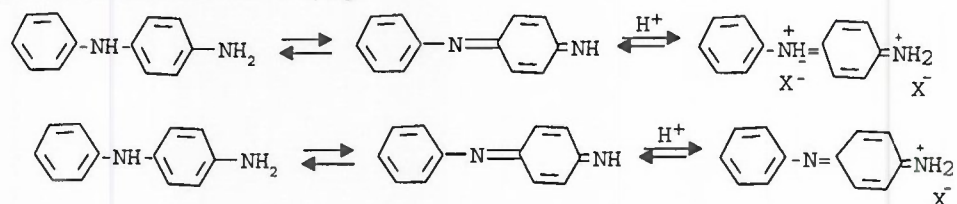
The formation of p-phenyl-1,4-phenylenediamine during the synthesis of aniline was proved earlier and it was found that the low fixed concentration of dimer during the synthesis remains constant in the abundance of aniline at the reaction medium [7]. In truth the method used by the authors shows the total concentration of the synthesized and reduced form of the dimer in the process of the synthesis, which is practically 2 degrees lower than the concentration of the monomer.

From the obtained results we can conclude that, the formatted dimer is not accumulated in reaction medium, but is oxidized in N-phenyl-1,4- benzoquinonediazine (Dq), which reacts rapidly to the aniline or other nucleophile. Such tests are not studied enough; however the chain reversible character of the interaction of the benzoquinone with the hydroquinone is approved [8].

We measured the size of the fixed concentration of the dimer based on the sense of the OR-potential of the equilibrium system and showed that the dimer after the formation practically completely changes into Dq, which reacts to aniline [9]. The kinetic investigations testify the changes of the mechanism of the reaction from the concentration of the proton. The increase of the speed of the polycondensation from the concentration of the proton and the fracture on the kinetic quinonediazine has trigonal atom of carbon (C=N) and therefore it is a stronger formation than the amine and in the acid medium it forms quaternary salt easier, while the capacity of electron-seeking increases during the transition of the amine into salt, which is formed at the interval of 2-3 mole/l concentration of proton where the fracture on the kinetic curve can be observed.

The obtained results along with the fixed concentration of the dimer in the process of the synthesis of polymers [7, 10] allow us to suggest that the formatted dimer inhibits the further oxidation of the aniline due to its low sense of OR-potential.

The primary estimation of the reaction equilibrium constant $A^+ + D \rightleftharpoons D^+ + A$ shows that the concentration A in the presence of D decreases for several degrees. The final product of the first step, basically, is the formation of the salt (Dq).



According to the results of the chromatographic analysis during the condensation of the aniline the accumulation of the oligomeric-soluble products occurs. At this step the formation of more than 6 products can be chromatographically fixed in the water medium. From the above mentioned products we could single out and identify, except earlier discovered D и Dq [11.12], 2,5-dianiline-phenylbenzoquinone-diamine (tetramer), 2,5-dianiline-N,N-diphenylbenzoquinone-diamine (pentamer). All these products are capable to form CTC with the aniline, which is accompanied by the appearance of the characteristic absorption of ultraviolet (UV) at 420 nm. The formatted diamine salt is a strong electron-seeking reagent and it reacts easily with the amine of the preliminary formation of CTC.

Thus the formation of the replaced quinoamines is reversible [13], occurring with the help of the isolation of protons, while in high acid medium aniline can be regenerated depending on its utilization.

It was shown that the speed of the isolation of the protons in the first stage increases by pH increase at the rate higher than the step of chain elongation.

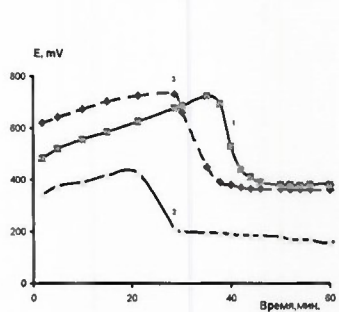


Fig. 1. The time-depending changes of the oxidative potential of the reaction medium. $[Ca] = 0.13$ mole/l, $[Cp] = 0.08$ mole/l; 1-in water, $[HCL] = 0.05$ mole/l, 2-in formic acid, 3-in water, in the presence of polyaniline 0.2g/l.

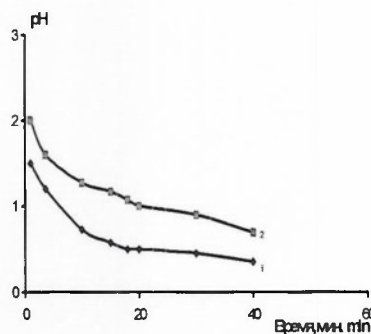


Fig. 2. The kinetic changes of pH of reaction medium $[Ca] = 0.13$ mole/l, $[Cp] = 0.08$ mole/l in water 0.05-0.1 HCL.

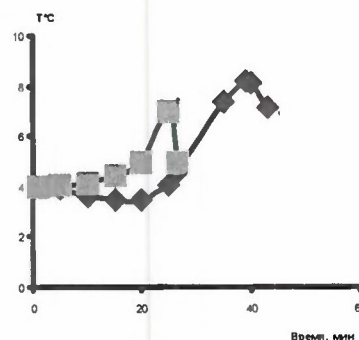


Fig 3. The temperature profile of the reaction $[Ca] = 0.13$ mole/l, $[Cp] = 0.08$ mole/l; 1-in water $[HCL] = 0.05$ mole/l, 2-in formic acid.

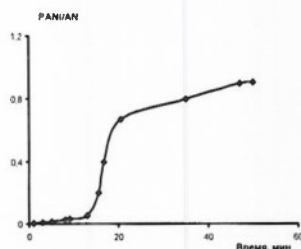


Fig. 4. The dependence of the polyaniline issue on the reaction time, $[Ca] = 0.13$ mole/l, $[Cp] = 0.08$ mole/l.

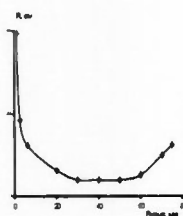
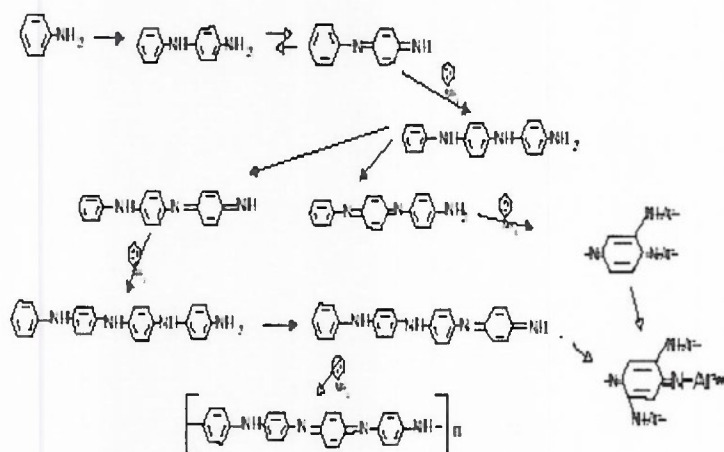


Fig. 5. The electroconductive changes of the polymer during the process of the synthesis, $[Ca] = 0.13$ mole/l, $[Cp] = 0.08$ mole/l

From the kinetic curves of the aniline oxidation by the ammonium persulphate (pic. 1-4) it is predicted that the maximum speed of the aniline oxidation is $3,67 \cdot 10^{-3}$ mole/l and it is increased almost by one degree ($1,39 \cdot 10^{-2}$) when 3mole % of dimer is added to the reaction system. We can also observe the increase of the speed of aniline oxidation when the reaction system is added by benzidine or polyaniline. In this case inhibition processes of the aniline oxidation by hydroquinone are not observed. The above mentioned results allow us to suggest that the slow stage of the increase of the polymer chain is the bonding process of the nucleophile-aniline with quinone, but not the reaction of the oxidation of dimer. From the obtained results the following mechanism of polyaniline formation is suggested:



which clarifies the possible ways of the formation of structural heterogeneities (defects) and the ways of optimal polymer synthesis with the preset properties.

Before synthesis, the aniline was vacuum dried, while difenylamine and carbazole and ammonium persulfate were used without additional clearing. The synthesis of polyaniline was carried out at concentration of aniline $[Ca] = 0,13 \text{ M/l}$ and ammonium persulfate $[Cp] = 0,08 \text{ M/l}$ in 0,1 and 0,05 M hydrochloric acid or in formic acid at 5°C .

Potentiometric measurements in water were carried out with the help of a platinum indicating electrode in a combination with calomel electrode of comparison. In a formic acid the kinetic measurements were carried out by a platinum electrode with the help of a glass electrode of comparison in buffer solution containing 10 g/l formic acid of lithium by the device "Ionomer FT-74". Kinetic studies were carried out also by a modified device EPR with working frequency of 9,4 GHz, frequency modulation- 100 kHz, the amplitude of modulation- 0,3 Hz. Cooled up to 0°C equal volumes of fresh solutions (0,3 M/l) of aniline and (0,3 M/l) of ammonium persulfate in formic acid were mixed in a quartz ampoule for 10-15 sec with, placed in resonator EPR and the measurements were carried out at 25°C .

Temperature profile of the process was obtained by measuring the temperature of the reactionary environment. After the reaction polyaniline was filtered, washed out by methanol, water, processed by 0,5 M solution of ammonia during 10 hours, washed out by water and dried during 7 hours at 50°C . For obtaining leucoemeraldine forms of polymer the samples were additionally processed by 1 M solution of hydrazine in water during 24 hours, washed out in water and dried in an inert atmosphere. The result was calculated as the ration of the synthesized polyaniline to the quantity of initial aniline.

The samples for measurement of relative resistance of polymer during the synthesis were prepared by drawing of 0,5 ml of reactionary suspension on the copper electrodes put on polythene and dried at 25°C during 24 hours and then at 50°C during 4 hours.

A thin layer chromatography of reactionary products was carried out on sylufol plates. For preparational purposes oligomeric products were divided chromatographically on a glass column with the carrier (silica gel or aluminium oxide) by a mix of solvents chloroform - methanol or acetone - toluene 1:1.

IR spectra of products of oxidizing polycondensation were obtained in tablets KBr, a for the films on substrates KBr or KRS glasses on the Fourier-spectrometer "Perkin Elmer 1600". The films were obtained by sedimentation of polymer on KRS glasses during the chemical synthesis or from a solution of purified emeraldine form of polymer in N-methylpyrrolidone, as well as by thermal vacuum sputtering on crystals KBr or quartz plates in an interval of temperatures $200-450^\circ\text{C}$ at the initial vacuum about 10^{-5} mm of mercury. The sputtering was carried out by sublimation of a powder from tungstic container. The control of temperature of the evaporator was carried out with the help of chromel-copel thermocouple fixed on the container. The sputtering was carried out in three stages, overlapping different temperature intervals, with reception of three fractions of films: $210 - 270^\circ\text{C}$ with preliminary warming of the container up to 210°C at closed screen during 10 minutes for clearing a powder; $270 - 350^\circ\text{C}$ and $350 - 450^\circ\text{C}$. The thickness of the films was measured by profilometer "Ambios XP-1".

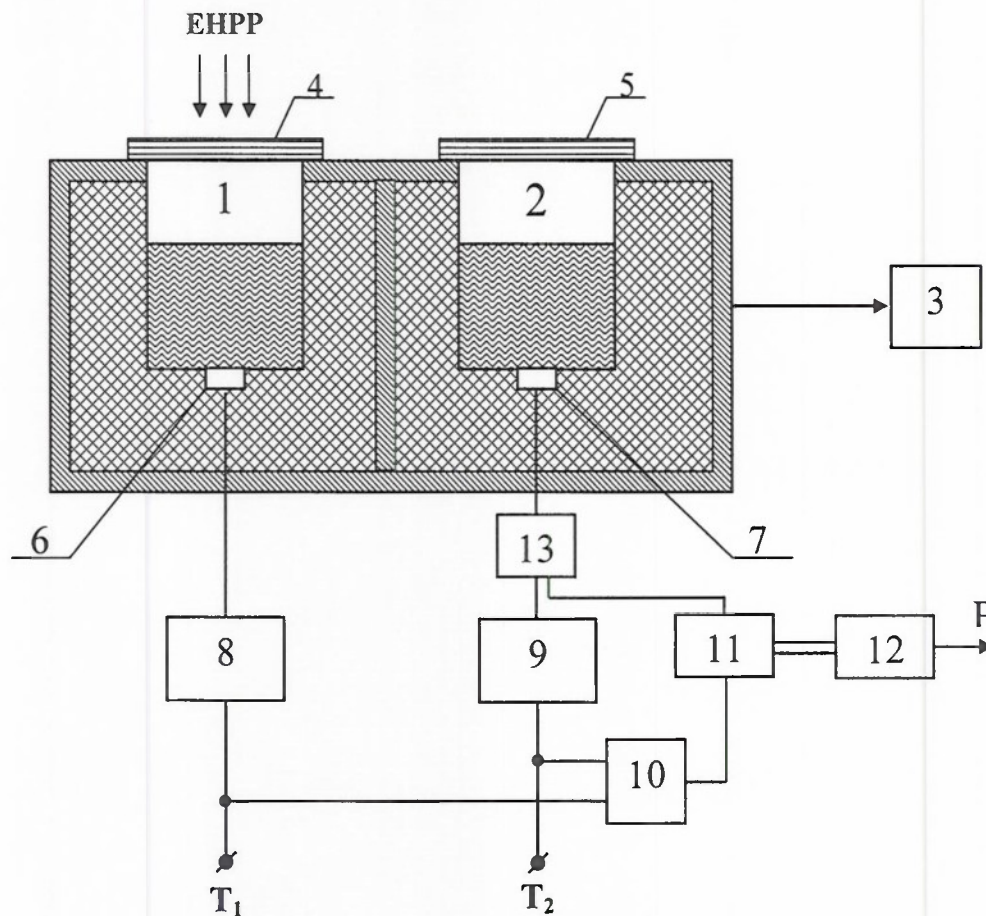
As the preliminary experiments on Extremely High Power Pulses (EHPP) effect on rats aimed to determine the lethal doses of EHPP exposure have given big variation between different animals, the latter made difficult to determine the exact shielding properties of new synthesized polymer films. Another reason for choosing a weaker intensity of MW, instead of EHPP, is for considerations of the security of the working personnel to hazardous effect of EHPP radiation on organism.

For determination of the MW radiation-induced biological effect on organisms, the water specific adsorption rate (SAR) was chosen instead of animal model. Such decision is authorized by the fact that the SAR of extracellular aqua medium determines the biological effect of MW on organism [Ziskin 2006; Ayrapetyan 2006] and it can be measured by micro-calorimeter and precisely estimate the shielding (adsorption) properties of new synthesized polymer films to MW radiation. For these purpose 260 GHz MW (modulated by 4 Hz EMF) was chosen, having intensity of 5,83 mW/cm². Such parameters of MW are used in clinics for therapeutic purposes [Ziskin 2006]. The SAR was estimated as

$$SAR = C_s \cdot \frac{\Delta T}{\Delta t} \Big|_{t=0}$$

where C_s is the specific heat of DW (4,168 J/g °C), ΔT - temperature changes in the result of MW radiation, Δt - expose time.

A setup for microcalorimetric measurements of polymer SAR was constructed on the basis of a microcalorimetric device "Biophys MWD-01" constructed at the Center. The scaled-down structural scheme of the devise is presented in Figure 4A & 4B.



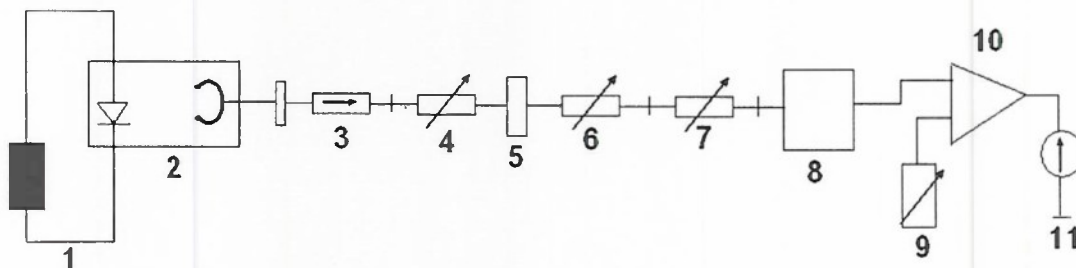
1. Measurement chamber
2. Comparison chamber
3. Thermostat

4. A cover transparent for the EHPP rays
5. Not transparent cover
6. Temperature transducer of the Measurement chamber
7. Temperature transducer of the Comparison chamber
8. Thermometer of the Measurement chamber
9. Thermometer of the Comparison chamber
10. Differential amplifier
11. Power amplifier
12. Power measuring system
13. Switching system

The device has the following technical parameters

- Thermometer of the Measuring Chamber 0-100 °C
- Thermometer of the Comparison Chamber 0-100 °C
- Error of temperature measurement $\pm 0,2$ °C
- Sensitivity of the thermometers of the Measuring Chamber 0,1 °C, with the capacity to amplify until 0,01 °C and 0,001 °C.
- Sensitivity of the thermometer of the Comparison Chamber 0,1 °C
- Range of the measurement of EHPP powers 0 – 199 mV.
- Admissible error of the measurement ≤ 2 mV.
- Power sensitivity 0,1 mV.
- Power supply from the alternating current 220 V/ $\pm 10\%$ 50Hz.

As the adsorption properties of polymers depends on EMF frequency, for estimation of this dependency, a special measuring setup for estimation of polymer films adsorption at 8,2 GHz MW radiation (intensity 30 mW/cm²), expressed in decibels (dB), was constructed. The figure scheme of this setup is presented on Figure 5A & B



1. Power supply
2. Generator on diode with output power 30 mW
3. Waveguide valve
4. Fixed Attenuator
5. Sample holder (measuring cell)
6. Precision alternating Attenuator
7. Fixed Attenuator
8. High precision radiometric device MP-3-7 (3 cm range)
9. Source of compensating voltage of the direct current
10. Differential amplifier of direct current
11. Magnet-electrical micrometer

The measurements are carried out by the method of substitution, when an unknown SAR of polymer material is determined by its substitution by its weakening in a known value.

The measurements are carried out as follows: after 30 minutes of switching the device on, for establishing the temperature regime of the generator and radiometer (the measuring cell is still empty),

the alternating Attenuator D5-2 is fixed in the position of maximal absorption. The fixed Attenuators provides the level of output voltage of the radiator about 0,1 W. Here we can record the indications of Attenuator 6 (the first indication).

With the help of source 7 of compensating voltage, with the regulating output voltage, we can obtain the zero bias of microcalorimeter 11. After which the polymer material is placed into the measuring cell and by lowering the weakening of Attenuator 6 we would again get zero bias on the output indicator 11. Then we obtain the new indications of the Attenuator (the second indication).

The differences between these indications 1 and 2 show the value of SAR of polymer material.

Such system provides:

- a/ High precision (error less than $\pm 0,5$ dB)
- b/ Quickness: each measurement is checked during about 15-20 min.
- c/ Exclusion of irradiation of the personnel during the measurements, as the waveguide section is completely covered.
- d/ The measurements could be carried out in a big range of absorption, because of the extrasensitivity of the radiometric device MP-3-7.

3. Results

The study of the process of synthesis of aromatic polyamines allowed us to find out the optimal conditions for the synthesis of polyaniline (PAN), polydiphenylamine (PDFA) and polycarbazole (PC), as well as to elaborate a new method of synthesis of copolymers with aminophenol, to simulate the conditions of formation of structural heterogeneity and to obtain the materials with the required quantity of heterogeneities (defects) for studying their characteristics.

The tests of the obtained samples have shown that PAN, then PDF, then PC have the most pronounced properties to absorb the MW radiation at 8.2 GHz.

At the frequency range of 260 GHz the more pronounced sorption properties have the polymer samples, which contain the heterogeneous (defects) structures, particularly OH-groups in the main chain of polyamines.

The obtained samples of conjugate aromatic polyamines differ by their high fragility and low solubility, which makes their treatment difficult.

The polymer films for the experiments were made under high pressure (400-600 kg/cm²). Therefore, the next task of our project was to develop the composites distinguished by their high flexibility and other characteristics. For this purpose we have elaborated modified polymers of aniline, which could combine with bounding polymers. The aniline polycondensation was performed in the medium, containing molecular modifiers like as PVC, PVB and others.

Table 1. The modified polymers of aniline (Nanokomposits)

Code	σ , (ohm cm) ⁻¹	η , dl/g	ΔK , dB	Δl , mm	$\Delta K/\Delta l$, dB	ΔT , °C	$\Delta T/(\text{Pb})$, %	SAR 10 ⁻⁴ mW/kg
8M-22	1,5/	0,4	15.5* 14.2**	1.0	14.2			
PAN-1	7.10 ⁻³	-	6.5 13.5	1	13.5	0.24	20	3.3
PAN-11	0.02 0.1 0.15	-	8.8 13,5 16-18					
8M-19	1,2	0,5	15-17.8 14.2	0,7	22	0,34	47-45	4,88
8M-20	1,0	0,45	12,5 13.2	-	-	0,03	35-40	4,19

8M-26	1,0	0,54	14.0					
8U 17	2,5	0,37	15-19 13.0	0,6	26	0,27	27-25	3,77
8 U 18	1,0	0,39	17-17.8 11.2	0,65	26	0,28	30	3,91
8M-21	1,5	0,3	12.5-16.2	0,8	18	0,031	35-37	4,33
8M-31	1,5	0,37						
PAN 320	10 ⁻³		6,5	0,6	10	0,024	20	3,35
6-52-4	10 ⁻⁵ 1.4 5.0		0.4 6.0 7.0					

* 8.8 GHz; ** 260 GHz

On Table 1 are represented the characteristics of the obtained modified polymers of aniline (Nanokomposits): specific electrical resistance (σ -ohm), adsorption 8,2 GHz MW in dB, and 260 GHz in SAR, Δl , thickness in mm

As can be seen from Table 1, the obtained samples have satisfactory properties, on the basis of which it is possible to develop compositional materials. Their modification allows us to obtain stable nanosized products. On the basis of the preliminary data we can conclude that the MW adsorption properties significantly depend on the morphology of samples, however this dependence is rather complicated and it needs more detailed investigation by more modern equipments, allowing to estimate the reflected and adsorbed components of MW radiation at higher and lower frequencies.

As the experiments showed, the modified aniline preserves its adsorption properties of MW radiation at the frequency of 8.2 GHz. The modification of polymers was performed in process of synthesis.

Our next step was to elaborate the elastic composites, containing modified polyaniline, polyacetylene and polycarbazole. The experiments in this work were mainly concentrated on the modified composites of PAN with polysilicon, polyurethane and poly vinyl- butyriral.

The composites were made in mixer and then the films or the plates were made by means of the standard polymer technology methods.

Some characteristics of the obtained composites are presented in Tables 2-4.

Table. 2 Composition polysilicone (PS) with modification.

Code	Compositi on	ΔK , dB	Δl , mm	$\Delta K/\Delta l$, dB/cm	ΔT , $^{\circ}C$	SAR, 10 ⁻⁴ mW/kg
K-S-8 Mod C	8 U17 PS AA	-	-	-		
K-S-9r Mod K+C $\sigma=1,2$	8 M19 PS, AA	9,8	1,8	6,5	0.021	2.93
K-S-9/1	8 M19; PS	9,8(14)			0.02	2.79
K-S-10r Mod PVC	8M-20 PS AA	7,2	1,8	4	0.034	4.74

K-S-10/1	8M-20 PS,	8,7	1,7	5,1	0.033	4.6
K-S-12 Mod PVB	8M-21 PS	9,1	0,7 8	11,6	0.036	5.2
K-S-13	8 U18 PS	9,3	1,5	6,2	0.032	4.47

(AA)-Acetic acid

As it can be seen from the presented data there is a reverse correlation between MW adsorption properties of silicon composites and diapering doping polymers. The obtained data show that in contrast to pure PAN, doping samples have more pronounced adsorption properties at 17-19 dB, and their modified samples obtained in the presence of polymer components show rather good results, which allows to use them in future as an elastic composites.

Table 3 Composition PS + mod-PAN- 11

Code	Composition, %	σ , (ohm sm) ⁻¹	ΔK , dB	Δl , mm	$\Delta K/\Delta l$, dB	ΔT , °C	SAR, 10 ⁻⁴ mW/kg
PAN-11	PAN+PVC+C	0.5	-16	1	16		
K-S-14	PAN-11, 45 PS	0.15	-5 10-13	1,3 0.7	5-6 17	0.036	5.02
K-S-15	PAN-11, 33 PS		-5 3	0,8 1	6,3 3	0.031	4.33
K-S-15r	PAN-11, 30 PS		-3,6 3.9	0,7 1.0	4,4 3.9	0.038 0.039	5.3 5.44
K-S-15r2	PAN-11, 26 PS		-2,6 2.2	0,8 0.9	2,8 2.5	0.036	5.02
PAN-1	PAN+PVC	7.10 ⁻³	13.5	1	13.5	0.24	3.3
K-S-4	PAN-1; 37 PS AA		3,2	1,3	2,5	0.021	2.9
K-S-5	PAN-1; 33 PS AA		2	1,9	1	0.019	2.65
K-S-7	PAN-1; 50 PS AA		4,3	1,3	3	0.03	4.19

The elaboration of butyric composites allows us to prepare the films by the method of filling, which is more reasonable.

Table 4. Polyvinilbutyric compositions +PAN.

Code	Composi tion/ %	σ , (ohm sm) ⁻¹	ΔK , dB	Δl , mm	ΔT , °C	SAR, 10 ⁻⁴ mW/kg
K-28	PAN-1 / 65	3,6 10 ⁻⁶	-2,5 -3		0.04	5.6 5.6
K-29	PAN-1 / 79	2,5 10 ⁻⁴	-4 -4,5		0.04	5.6
K-30	8M26 / 63	3,8 10 ⁻²	-5 -5.7		0.04	-6.14
K-31	8M26 / 2.2	10 ⁻⁸	0		-	

K-32	8M19 / 16	$1,4 \cdot 10^{-8}$	0	1	0.039	5.44
K-32	8M19 / 16	$1,4 \cdot 10^{-8}$	-1.5	2		
K-32	8M19 / 16	$1,4 \cdot 10^{-8}$	-1.5	3		
K-33	8 U18 / 13	$\sigma \rightarrow 0$	0	1-4	0.036	5.02
K-34	8M20 / 8	$\sigma \rightarrow 0$	-0,5-1,5 0		0.05	7.0 -6.98
K-35	8 U 17 / 5	$\sigma \rightarrow 0$	0	1-4	0.045	6.28

The obtained data show that the adsorption properties of the samples are increased by the elevation of the content of PAN in compositions and by the growth of electrical conductivity. Those composites, which contain 30% of PAN, give homogenous films, while in case of more than 50% of PAN fragile powder, able to compress in the plates. The modified PAN allows us to prepare composites, the 80% of the component of which is conjugate polymer.

Table 5. Polyurethane composition

Code	Compositi-on, %	ΔK , dB	Δl , mm	$\Delta K/\Delta l$, dB/mm	ΔT , °C	ΔT , % propusk Pb	SAR 10^{-4} mW/kg
K-U	Polyuretan 100	0	1,5	0	0.053	90	7.26
K-PU	PAN; 0	0	2,0	0	0,052	90	7,14
K-2	PAN 1; 38	-3,7	1,8	2	0,025	22,5	3,5 4.74
K-3	PAN-1; 36	-5,7	1,4	4	0,028	30	3,91
K-1	PAN-1; 33	-3,2	0,8	3,7	0,035	47,5	4.88
K-19	PAN-11; 25	-	-	-	-	-	-
K-19-1	PAN-11; 18	-0,8-1,5	1,7	0,8	0,026	25	3,63
K-19-2	PAN-11; 40	-5.9			0.04	60	5.58
K-20	PAN-11;16	-1,5-2,2	0,5	4,4			4.2
Thin layer coating paints							
K-16	PAN-11; 62						
K-17	PAN-11; 45	0	0,3	0	0,022	15	3,1
K-18	PAN-11; 33						

The polyurethane compositions are characterized by high adhesion properties.

In addition to our present project, the aim of which is to obtain more acceptable technological products with high MW absorption properties, we have developed liquid coloring stuffs, containing the modified PAN, which can be used to cover the protective surface just by brushing or by compressed air spraying. As the experiments showed these composites have high MW absorption properties at the frequency of 260 GHz, while at the frequency of 8.2 GHz the rate of the absorption properties is low. The optimal components of the obtained conjugated polymers and their composites, as well as the methods of their production can be presented for patenting. These composites can be produced with the necessary amount by standard equipment used for the obtained polymers.

4. Conclusion

In the present project for the first time the polyaniline, polydifenilamine, polycarbazole of the set structure (including functional groups) and morphology of nano-sized particles with the optimal radiowaves absorption rate was elaborated. From the obtained semiconducting polymers, elastic and flexible composite materials including nano-composites were developed. We find out that the silicon compositions and nano-sized compositions have the highest adsorption properties. We suggest that the development of these nano- sized compositions and their derivatives is very promising from the point of obtaining new coating materials, having higher adsorption properties. However, in the framework of

present project, our technical possibility did not allow us to study their adsorption properties at different frequency of modulated and non-modulated MW, as well as their multisided physicochemical and structural characteristics.

For the study of MW adsorption properties of synthesised polymers film a new microcalorimetric and radiometric methods were elaborated. However, for obtaining more precise data on specific adsorption rate of MW at different frequency for different materials these new methods need the future modification.

For estimation of the protective (shielding) properties of organisms from non-thermal biological effect of MW, two extrasensitive methods were used: a) luminicent method measuring the hydrogen peroxide (H_2O_2) formation in shielded and non-shielded water samples and b) isolated snail heart muscle contractility.

Thus, by performing the present project it was established the necessary theoretical chemo-technical basis for synthesis of aromatic polymers and for studying their MW adsorption properties from the point of public health. Further development of this project could allow to create and improve the technology of synthesis and properties of synthesised polymers that could be applicable for protection of electronic communications from unauthorized invasions, for companies producing mobile phones and, generally, radio electric equipment. Thin-film compositions could be used for camouflage of land, marine and air objects.

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Attachement 1

List of published papers and reports with abstracts

1. Matnishyan H.A, Vardanyan AO., Hakhnazaryan T.L, Khachatryan SD., Artsruni GV., Amirganyan R.S, Abaghyan G.V, Petrosyan SI., Hambartsumyan G.V. 2008. Formation of structural inhomogenities and branchings at synthesis of polyaniline and film creation, Armenian Journal of Chemistry 2008, 61(1): 119-128.

Abstract.

Conformities of synthesis of polyaniline in water and formic acid are investigated. Kinetics of an aniline oxidized by disulphate of ammonium were measured by potentiometric and thermochemical methods. The process of synthesis was controlled both by output and change of conductance of the polymer. Three main stages of the process are established: at first the accumulation of oligomeric quinonimides, then the growth of chain takes place, which is carried out by addition of aniline to quinonimines groups, the third stage is the postpolymerization. The oligomeric intermediate products- the substituted quinonimines are separated. On the basis of the analysis of IR and NMR spectra both three- and tetra- substituted aromatic groups and fenazine structural units in a chain of polyaniline are detected. The branching structure of polyaniline is proposed.

Thin films (100-800nm) of polyaniline are investigated. It was shown that at temperature of 250-350°C the sewing appeared and the formation of fenazine structural fragments took place. At higher temperatures of vacuum evaporation, the polymer practically is nonsoluble and there are new fragments of hetheroaromatic structures: three- and tetra- substituted aromatic cores.

2. Zhubanov B.A., Kravtsov V.D., Iskakov R.M., Matnishyan H.A. 2008. Polymer composites on the basis of alicyclic polyimides and electroconductive polymers. Journal of applied chemistry (in press)

Abstract. The composites of polyaniline with polyimides were synthesised and the properties of the obtained materials were studied.

Attachement 2

List of presentations at conferences and meetings with abstracts

Matnishyan H.A., Hakhnazaryan T.L., Grigiryan A.R., Artsruni G.V., Hakobyan M.I. The mechanism of oxidative polycondensation of aromatic amines. Plenary lecture at International Seminar "Modern approaches in Polymer Chemistry" Almaty (Kazakhstan) 9-10 October 2008.

Abstract:

Among semiconducting materials, polyaniline possesses the most practical interest. Its synthesis with the controlled structural heterogeneities is rather complicated process the mechanism of which is purely investigated. We have shown that such structural heterogeneities appeared during the synthesis and suggested a mechanism of oxidative polycondensation of polyaniline.

Matnishyan H.A., Hakhnazaryan T.L., Khachatryan S.D., Grigiryan A.R., Artsruni G.V., Hakobyan M.I. Plenary lecture "The modern problems of chemical sciences in Armenia", The 1st Seminar of Armenian chemical society. 17-18 June 2008, Yerevan, Armenia

Abstract

We showed which such structural heterogeneities appear during the synthesis and suggested a mechanism of oxidative polycondensation of polyaniline.

Matnishyan H. A., Hakhnazaryan T.L. Organic semiconducting materials (aromatic polyamines): synthesis, properties and perspectives of their application for protection from High frequency radiation. UNESCO/ONRG Seminar: "Electromagnetic Fields: Mechanisms of Action and Health Effect" 24-26 October 2008, Yerevan, Armenia

Attachement 3

Information on patents and copy rights

The preparation of patent application in collaboration with our partners is planned.